

158-263-62

Finite-Mass Helium Atoms II. The 2^3P State⁺

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GPO PRICE \$

The University of Texas

CFSTI PRICE(S) \$

Austin, Texas 78712

Hard copy (HC)

1.00

Microfiche (MF)

.50

ABSTRACT

ff 653 July 65

29426

The 2^3P states of the helium isoelectronic series are investigated via 50-term variational wavefunctions containing two nonlinear parameters. The Hamiltonian, spin free and non-relativistic, is written directly in center-of-mass coordinates so that no adiabatic approximation is required. The expectation values of the Hamiltonian and of moments of the interparticle separations are reported. Isotope shifts are found, and, as noted in a preliminary report, are in excellent agreement with experiment. In order to compare the results with previous theoretical results the systems were similarly studied in the infinite nuclear mass limit (adiabatic approximation). The energies so obtained are the deepest so far obtained by a direct calculation with a variational wavefunction. The expectation values of the operators were subjected to a differencing process to obtain estimates of the perturbation expansion coefficients for them, and the results are in good agreement with the directly calculated results of Knight and Scherr.

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⁺This research was supported by a grant from the National Aeronautics and Space Administration.

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I. INTRODUCTION

In paper I the 2^1P states of the helium atom iso-electronic series were treated by a variational procedure in which the Hamiltonian explicitly contained the correct mass dependence (true mass calculation)¹. Studies were also made of these states in the infinite nuclear mass approximation (adiabatic approximation). The true mass calculation results were used to study the isotope-shifts in these systems, thus providing a direct link with experiment. As a further indication of the reliability of the calculations, the infinite mass calculation results were analysed and a comparison made with some results of perturbation theory. The work started in Paper I is completed here with a similar set of calculations for the 2^3P states of the same systems.

The comparison of the infinite mass calculation results with the results of perturbation theory is achieved through a well-known consequence of the Schrödinger perturbation procedure: for atomic systems the total wavefunction Ψ can be written as an expansion in inverse powers of the nuclear charge Z . Consequently, expectation values of any operator Ω are obtained in a power series in Z^{-1} :

$$\int d\tau \Psi \Omega \Psi = \langle \Omega \rangle = \sum Z^{a-n} \langle \Omega \rangle_n, \quad (1)$$

where the value of a depends on the nature of the operator Ω .

The Ψ is assumed to be real and to be normalized. In particular, the expectation value of the Hamiltonian is the total energy, $E(Z)$,

$$E(Z) = Z^2 \sum Z^{-n} \epsilon_n. \quad (2)$$

It is usually easy to compute the lead coefficient in Eqs. (1) and (2) by an elementary integration, and in a number of cases the next few coefficients have been numerically approximated.² In addition, it is known that³

$$2\langle r^{-1} \rangle_n = (n-2)\epsilon_n, \quad (3)$$

$$\langle u^{-1} \rangle_n = (n+1)\epsilon_{n+1}, \quad (4)$$

where r is the electron-nucleus separation, and u is the electron-electron separation. Estimates of the leading coefficients in Eqs. (1) and (2) may be obtained from the results of a series of variational calculations via a differencing technique that regards the data as truncated expansions of the form of Eq. (1).

II. RESULTS

The value of the lowest energy found for each value of Z considered is displayed in Table I for both the infinite mass calculations and for the more common or stable isotopes of the atoms. (These calculations do not give a stable 2^3P state for H^- .) From these data and from the Rydberg values in Table II of paper I, isotope shifts are calculated and presented in Table II. The perturbation energy expansion coefficients were recovered from $E_2(Z)$. For Z from 2 to 10 inclusive, where $E_2(Z)$ is defined by

$$E_2(Z) = E(Z) + (5/8)Z^2 - (1481/6561)Z$$

for the 2^3P systems, the results are presented in Table III.

Total expectation values of the moments of the interparticle coordinates are also computed. As in Paper I, these data are analysed via the differencing technique in two ways: (1) direct analysis of the basic data, (2) analysis of the data after removal of the exactly-known zero order coefficient. The first way gives results substantially similar to the results of the analysis of the 2^1P data, and they are not reported. The results of the second way are presented in Table IV. In addition, a third analysis is performed: (3) analysis of the $\langle r^{-1} \rangle$ and $\langle u^{-1} \rangle$ data after removal of the exactly-known zero-order coefficient and of the first-order coefficient, known via Eqs. (3) or (4). The $\langle r^{-1} \rangle_1 = -1/2\epsilon_1$ is known exactly, while the $\langle u^{-1} \rangle_1 = 2\epsilon_2$ is taken from reference 2, where it has been numerically obtained to more significant figures than are needed here. The results of this third analysis are presented in Table V not only for the 2^3P states but also for the 2^1P states.

III. DISCUSSION

Pekeris, Schiff and Lifson³ employed a 220-term variational wavefunction in a study of 2P and 3P states of the helium atom. Their energy result⁴ for the infinite mass helium 2^3P state is -2.1331633 a.u. As in paper I, the deeper energy of the 50-term wavefunction used here is to be attributed to the fact that Pekeris, Schiff and Lifson preselected their non-linear parameters. Their 3^3P energy value is -2.0580715 a.u., and the 50-term value is -2.0563023 a.u.

As in the 2^1P calculations, the extrapolation of the non-linear parameters to the case of infinite Z is not clearcut because of multiple minima. Approximately, they extrapolate to $1.018Z$ and $0.62Z$ and the Pekeris, Schiff and Lifson values to Z and $0.5Z$ correspondingly. (The 2^1P 50-term values extrapolated to $1.005Z$ and $0.64Z$.)

The isotope shifts for Z equals 2 and 3 calculated in this note have already been discussed elsewhere.⁵ The results for the isoelectronic series, presented in Table II, can be roughly fitted to an expression whose leading terms are

$$\text{Shift (cm}^{-1}\text{)} = 1.03 \times 10^4 Z^2 m\mu^{-1}(1 - 1.50Z^{-1} + \dots)$$

where μ^{-1} is the magnitude of the difference of the reciprocal masses of the two nuclei involved and m is the electronic mass. If the shift is calculated from a simple, properly symmetrized, product wavefunction of the type considered by Hughes and Eckart,⁶ but using the Pekeris et al prescription for the orbital exponents, then the result is

$$\text{Shift (cm}^{-1}\text{)} = 1.00 \times 10^4 Z^2 m\mu^{-1} (1 - 1.51 Z^{-1} + \dots).$$

FOOTNOTES

1. M. Machacek, F. Sanders, and C. W. Scherr, in press.
2. R. E. Knight and C. W. Scherr, Rev. Mod. Phys. 35, 431(1963).
3. C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. 126, 1057 (1962).
4. Pekeris, Schiff and Lifson also present extrapolated results which should be very accurate. These are, for the 2^3P state, -2.1331641 a.u. and for the 3^3P state, -2.0580812 a.u.
5. M. Machacek and C. W. Scherr, J. Chem. Phys. 39, 3151(1963).
6. D. S. Hughes and C. Eckart, Phys. Rev. 36, 694(1930).

TABLE I
THE ENERGIES IN REDUCED ATOMIC UNITS^a

Isotope	(m/M)x10 ⁴	E(true mass)	E(infinite mass)
He ³	1.8192	-2.13317527	-2.13316352
He ⁴	1.3706	-2.13317237	
Li ⁶	0.9126	-5.02774288	-5.02771503
Li ⁷	0.7821	-5.02773889	
Be ⁹	0.6089	-9.17501548	-9.17497248
B ¹⁰	0.5480	-14.5732063	-14.5731370
B ¹¹	0.4984	-14.5732000	
C ¹²	0.4573	-21.2218005 ⁻	-21.2217100
C ¹³	0.4220	-21.2217935 ⁻	
N ¹⁴	0.3919	-29.1206127	-29.1205010
N ¹⁵	0.36585	-29.1206053	
O ¹⁶	0.3431	-38.2695549	-38.2694219
O ¹⁷	0.3228	-38.2695471	
O ¹⁸	0.3049	-38.2695401	
F ¹⁹	0.2888	-48.6685726	-48.6684265 ⁻
Ne ²⁰	0.2745	-60.3176636	-60.3174880
Ne ²¹	0.2614	-60.3176553	
Ne ²²	0.2495	-60.3176476	

^aReduced atomic energy units in units of $\mu e^4 \hbar^{-2}$. Let m be the mass of the electron and M be the mass of the nucleus, then the reduced mass, $\mu = mM/(M+m)$. For the infinite mass systems $\mu = m$, and the Rydberg is the familiar infinite mass Rydberg.

TABLE II
ISOTOPE SHIFTS

Systems	Shift (cm ⁻¹) ^a
He ³ ; He ⁴	0.675 ± 0.005
Li ⁶ ; Li ⁷	0.633 ± 0.006
B ¹⁰ ; B ¹¹	0.88 ± 0.05
C ¹² ; C ¹³	0.96 ± 0.06
N ¹⁴ ; N ¹⁵	1.00 ± 0.06
O ¹⁶ ; O ¹⁷	1.07 ± 0.07
O ¹⁶ ; O ¹⁸	2.00 ± 0.07
Ne ²⁰ ; Ne ²¹	1.13 ± 0.08
Ne ²⁰ ; Ne ²²	2.14 ± 0.08

^aThe error estimate is the same as was made for the corresponding data of the ¹P states.

TABLE III
THE ϵ_n IN ATOMIC UNITS

n	Recovered here ^a	Knight and Scherr ^b
2	-0.072997	-0.072992603
3	-0.01661	-0.016558519
4	-0.01013	
5	-0.0065 ⁻	

^aThe Z = 2 and 3 values are not included in the analysis. The last digit is to be regarded as unreliable.

^bData from reference 2.

TABLE IV
RECOVERY^a OF THE $\langle \Omega \rangle_n$

Ω	$\langle \Omega \rangle_0$	$\langle \Omega \rangle_1$	$\langle \Omega \rangle_2$
r^{-1}	5/8	-0.11251	0.00409
r	13/4	1.969	1.681
r^2	33/2	23.99	24.7 ₇
u^{-1}	1481/6561	-0.14469	-0.06620
u	70615/13122	3.677	3.19 ₇
u^2	2014153/59049	48.1 ₇	48.6 ₇

^aThe $Z = 2$ and 3 values are not included in the analysis.

TABLE V
A REFINED RECOVERY^a OF $\langle r^{-1} \rangle_n$ AND $\langle u^{-1} \rangle_n$

State	Ω	$\langle \Omega \rangle_0$	$\langle \Omega \rangle_1$	$\langle \Omega \rangle_2$	$\langle \Omega \rangle_3$
1_p	r^{-1}	5/8	1705/13122	-0.0005_0	0.01604
1_p	u^{-1}	1705/6561	-0.31404246^b	0.0787	0.0131
3_p	r^{-1}	5/8	1481/13122	0.0006_6	-0.0145_1
3_p	u^{-1}	1481/6561	-0.145985206^b	-0.0490	-0.0518

^aThe Z = 2 and 3 values are not included in the analysis.

^bData from reference 2.